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# Photosensitizer efficacy of non-peripheral substituted alkylbenzopyridoporphyrazines for photodynamic therapy of cancer

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## Abstract

The triplet state of zinc non-peripheral substituted alkylbenzopyridoporphyrazines and position isomers were measured, using laser-flash photolysis in poly(methyl methacrylate) film. The triplet lifetime increased with an increasing pyridine number in the molecule. The lowest symmetric isomer having two pyridine rings in the molecule showed the longest triplet state lifetime. The compound was suitable for the use the photosensitizer as a photodynamic therapy of cancer.

*Keywords:* Zinc phthalocyanine derivatives; Alkylbenzopyridoporphyrazine; Photodynamic therapy of cancer; Laser-flash photolysis; Poly(vinyl alcohol) coating

## 1. Introduction

Phthalocyanine derivatives have been utilized in important functional materials in the last decade for photoconductors [1], and have been attracted to the photodynamic therapy of cancer (PDT) [2]. Especially, aluminium and zinc phthalocyanine derivatives are expected to be used as the photosensitizer for PDT [3]. In these days, porphyrin derivatives such as hematoporphyrin derivatives and Photofrin™ have been used as photosensitizers for PDT at medical institutions [4,5].

In general, the sensitizer for PDT requires a high photostability, high selectivity to tumors, no cytotoxity when no light is irradiated, strong absorption in the region between 600 and 800 nm where penetration of tissue is good, and a long triplet state lifetime [6]. However porphyrin derivatives including hematoporphyrin derivatives and Photofrin™ are known to have a main absorption of around 400 nm where tissue penetration is low and a weak absorption. On the other hand, phthalocyanine derivatives exhibit the maximum absorption in the far-red range between 600 and 850 nm, and have a greater penetration of tissue [7] and a long triplet lifetime, and high singlet oxygen quantum yields [8]. The aggregation properties of phthalocyanine derivatives are a strong influence on the bioavailability, the in vivo distribution and the oxygen production efficiency [9].

In spite of their properties, there are few reports involving use of sensitizers for PDT because of their low level of solubility in common organic solvents. Naturally, many studies are making efforts to the syntheses of soluble metal phthalocyanine derivatives [1]. In order to be soluble in an aqueous media, the introduction of substituents such as sulfo and fluoro groups were performed and reported [1,6,10,11]. For instance, sulfonated chloroaluminium phthalocyanine derivatives were potent sensitizer for PDT [10,11]. Sulfonated zinc phthalocyanine derivatives were also studied for PDT [6].

Phthalocyanine analogues containing a pyridine ring in place of one or more of the benzenoid rings are interesting compounds because quaternation of the pyridine nitrogen is expected to confer solubility in an aqueous media [12]. Then, tetramethylated tetrapyridoporphyrazines by quaternation became soluble in an aqueous media, and then

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these compounds were studied for PDT [13]. Meanwhile, lipophilic phthalocyanine derivatives having alkyl groups are reported to have a higher tumor affinity [14].

In this paper, the authors report the triplet state of a non-peripheral substituted phthalocyanine derivative, zinc dibenzo-di(3,4-pyrido)porphyrazine in polymer layer, which is one of a fundamental model of a cell using laser-flash photolysis. Of course, we know that PMMA films are not suitable enough to the model of a cell and liposome is conformed for the purpose. However, since PMMA is conveniently and inexpensively available, and liposome is a very expensive material, we have used the compound which was the model of cell in the first stage of the study. Moreover, there are a few reports where the laser-flash photolysis of a sensitizer for PDT were performed for solids or films, so PMMA was used as a basic material for the study. Introducing long alkyl-chain substituents in the molecule can increase their solubility in organic solvents. The phthalocyanine derivative exhibits solubility in organic solvents and is expected to have a higher tumor affinity. On the other hand, the phthalocyanine derivative containing pyridine rings is expected to be soluble in water by quaternation. The aggregation of photosensitizers is thought to reduce their photodynamic activity [6,8]. Although the long alkyl-chain substituents in the molecule occur in aggregation, the phthalocyanine derivative is expected to undergo rapidly photodecomposition after the photooxidation process. The photosensitizer should be made in isomerically pure form [8]. Therefore, since we reported the synthesis and the isomer separation of non-peripheral substituted zinc dibenzo-di(3,4-pyrido)porphyrazine [12], we also examined laser-flash photolysis of the isomers in a polymer layer.

## 2. Experimental

### 2.1. Equipment

Ultraviolet-visible (UV-Vis) spectra were measured on a Shimadzu UV-2400PC spectrometer. Each sample was prepared in toluene at $5.0 \times 10^{-5}$ mol dm$^{-3}$, except for the toluene-insoluble sample (the insoluble sample was prepared in pyridine at $2.6 \times 10^{-5}$ mol dm$^{-3}$). Fluorescent spectra were recorded in *N*,*N*-dimethylformamide (DMF) on a Hitachi F-4500 fluorescence spectrometer.

### 2.2. Alkylbenzopyridoporphyrazines [12]

We synthesized three types of alkylbenzopyridoporphyrazines, which have different numbers of pyridine rings in the molecule (Fig. 1) [12]. Zinc 1,4-didecylbenzo-*tris*(3,4-pyrido)porphyrazine (**1b**), zinc bis(1,4-didecylbenzo)-bis-(3,4-pyrido)porphyrazine (**1c**), zinc *tris*(1,4-didecylbenzo)-3,4-pyridoporphyrazine (**1d**) were synthesized from mixtures of 3,6-didecylphthalonitrile [15] and 3,4-dicyanopyridine [12] for 3 (0.18 g, 0.30 mmol):1 (0.02 g, 0.15 mmol), 1 (0.12 g, 0.29 mmol):1 (0.04 g, 0.29 mmol) and 1 (0.06 g, 0.15 mmol):3 (0.06 g, 0.45 mmol) ratio, respectively. Each mixture was dissolved in pentanol (7 ml) and zinc chloride (0.05 g) was added. The mixture was heated for 4 h in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene as a catalyst. After cooling, the reaction mixture was dissolved in toluene (50 ml) and the solution filtered. The solvent was removed by evaporation. The products were purified by chromatography (eluent: toluene). Zinc tetra-3,4-pyridoporphyrazine (**1a**) and zinc octadecylphthalocyanine (**1e**) were synthesized from 3,4-dicyanopyridine and 3,6-didecylphthalonitrile, respectively. These compounds were analyzed and characterized by infrared, proton magnetic resonance and UV-Vis spectra, elemental analysis, and cyclic voltammetry [12] (Scheme 1).

### 2.3. Separation of position isomer [12]

The position isomers of the compound, **1c** were separated into four green- to blue-colored fractions using TLC (Merck Silica gel 60 $F_{254}$ on an aluminium sheet, eluent—toluene:pyridine 7:3). These fractions were numbered as 1, 2, 3 and 4, according to the $R_f$ values, and the $R_f$ values were 0.95, 0.91, 0.75 and 0.65, respectively. Each fraction was recovered by scraping from the TLC plate, dissolved in pyridine, the solution filtered, and the solvent removed. The total amounts of fractions 1–4 are 26.1, 17.4, 17.4 and 39.1%, respectively. Fractions 1–4 are assigned as $D_{2h}$, $C_{2h}$, $C_s$ and $C_{2v}$ (Fig. 2). The detailed data about the separated isomers were described in the literature [12].

### 2.4. Laser-flash photolysis

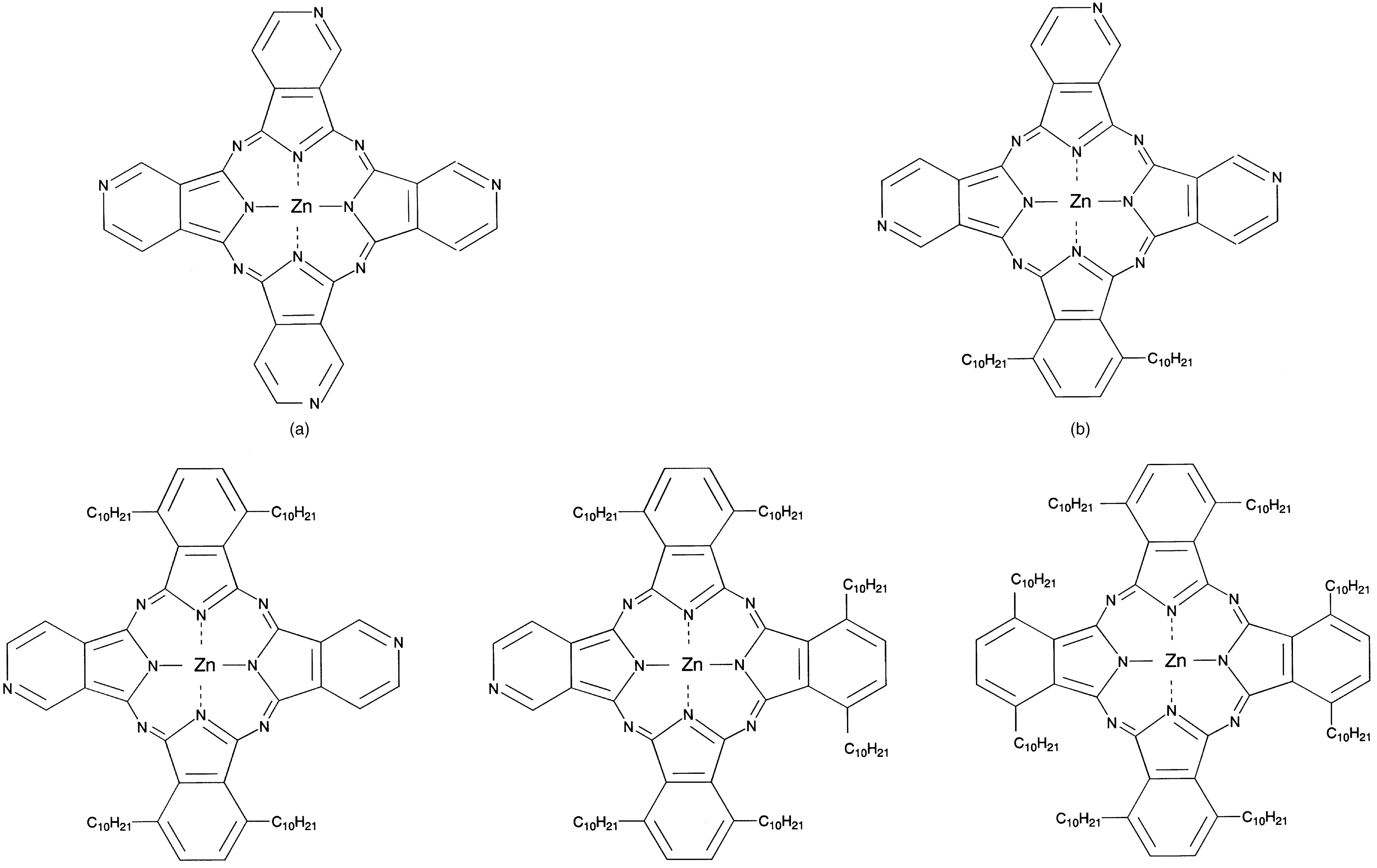
Laser-flash photolysis in film was performed using a total reflection sapphire cell (10 × 30 mm, 1 mm thick, and both of the short side were cut at a 45° angle), which was spin-coated with a 1.2 μm thick photopolymer film. An excitation light pulse (20 ms, 355 nm and 10 mJ/pulse) from a YAG laser was expanded and exposed over the entire sample cell. A monitoring light from a xenon lamp passed through the multireflection cell which was connected to the head of an optical fiber attached to a monochrometer equipped with a photomultiplier or to a spectral multichannel analyzer system.

The films were prepared as follows: a 10 wt.% poly(methyl methacrylate) (PMMA) solution was made up in cyclohexanone, allylbenzopyridoporphyrazines were added to this solution by dissolving to a thickness of 1.2 μm thick by spin-coating a solution onto a sapphire cell. After that the films were covered with a poly(vinyl alcohol) (PVA) solution.

## 3. Results and discussion

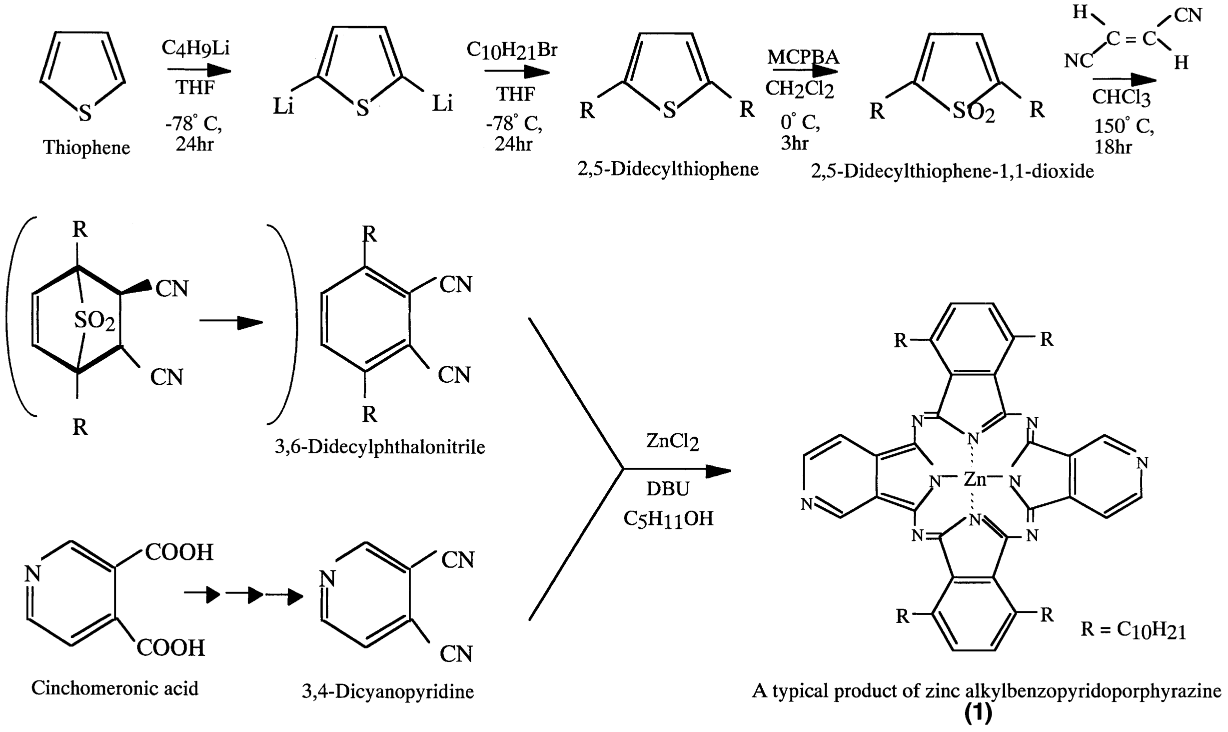
### 3.1. Alkylbenzopyridoporphyrazine

Fig. 3 shows UV-Vis spectra of **1a** and **1c** in toluene at $5.0 \times 10^{-5}$ mol dm$^{-3}$, and **1e** in pyridine at 2.6 ×



(a) (b) (c) (d) (e)

Fig. 1. Molecular structures of zinc tetra-3,4-pyridoporphyrazine, zinc alkylbenzopyridoporphyrazines and zinc octadecylphthalocyanine. **1a**: Zinc tetra-3,4-pyridoporphyrazine; **1b**: zinc 1,4-didecylbenzo-*tris*(3,4-pyrido)porphyrazine; **1c**: zinc bis(1,4-didecylbenzo)-bis(3,4-pyrido)porphyrazine; **1d**: zinc *tris*(1,4-didecylbenzo)-3,4-pyridoporphyrazine; **1e**: zinc octadecylphthalocyanine.



**(1a)**; Zinc tetra-3,4-pyridoporphyrazine,
**(1b)**; zinc 1,4-didecylbenzo-tris(3,4-pyrido)porphyrazine,
**(1c)**; zinc bis(1,4-didecylbenzo)-bis(3,4-pyrido)porphyrazine,
**(1d)**; zinc tris(1,4didecylbenzo)-3,4-pyridoporphyrazine,
**(1e)**; zinc octadecylphthalocyanine.

Scheme 1.

$10^{-5}$ mol dm$^{-3}$. The absorption maxima of the compounds appeared around 660–710 nm in the solutions. The UV-Vis spectra of **1a**, **1c** and **1e** show the typical shape for phthalocyanine derivatives. The strongest peaks are assigned as the Q-band, which could be attributed to the allowed $\pi$–$\pi^*$ transition of a phthalocyanine ring. The absorption maxima ($\lambda_{max}$) and log $\varepsilon_{max}$ of products are summarized in the table of Fig. 3. As shown in the table of Fig. 3, the **1c** had the strongest absorption intensity of the products. Fig. 4 shows the time profiles of the triplet state for one of the alkylbenzopyridoporphyrazines, **1c** in PMMA was observed using laser-flash photolysis.

The triplet state lifetime of alkylbenzopyridoporphyarazines, **1b**–**1d** and **1e** were summarized in Table 1. In each alkylbenzopyridoporphyrazine, it is shown that **1b** and **1c** have longer triplet lifetimes than **1d** and **1e**. The length of the triplet lifetime for alkylbenzopyridoporphyrazine depends upon its molecular structure. The triplet lifetime of alkylbenzopyridoporphyrazines increased with increasing pyridine numbers in the molecule. It seems that if tetrapyridoporphyrazine **1a** can be soluble in common solvents and measured for laser-flash photolysis, its triplet lifetime will be shown the longest value.

The photoexcited triplet state lifetimes of **1b** and **1c** in PMMA without a PVA coating were estimation to be 11.4 and 10.1 μs, respectively. While covered with a PVA coating, the photoexcited triplet state lifetimes of **1b** and **1c** were estimated as 51.8 and 46.9 μs, respectively. Compared with each compound, the triplet state lifetime in PMMA covered with PVA was longer than without the PVA coating.

The Q-band absorption of alkylbenzopyridoporphyrazines in PMMA films was similar to that in solution, but the profile of Q-band in PMMA film became wider than that in solution and moved to a longer wavelength, except for **1e**.

Non-transition metal phthalocyanine derivatives were known to be excellent photosensitizers because of their chemical stability and high absorbance in the 650–700 nm region [16]. In the presence of a photosensitizer, photooxidation progresses via singlet state oxygen [17–27]. Phthalocyanine derivatives in the excited triplet state react with ground triplet state dioxygen. The triplet state dioxygen generated singlet excited state oxygen. The singlet excited oxygen reacts with a substrate to produce oxide (Eqs. (1)–(3)) [12,13]

$$\text{M-PC} \xrightarrow{h\nu} {}^{1}\text{M-PC} \xrightarrow{\text{intersystem crossing}} {}^{3}\text{M-PC} \qquad (1)$$

$$ {}^{3}\text{M-PC} + {}^{3}\text{O}_2 \rightarrow \text{M-PC} + {}^{1}\text{O}_2 \qquad (2)$$

$$ {}^{1}\text{O}_2 + \text{substrate} \rightarrow \text{substrate oxide} \qquad (3)$$

Both, covered with a coating and without PVA, the photooxidation proceeded as the same mechanism. However, in the

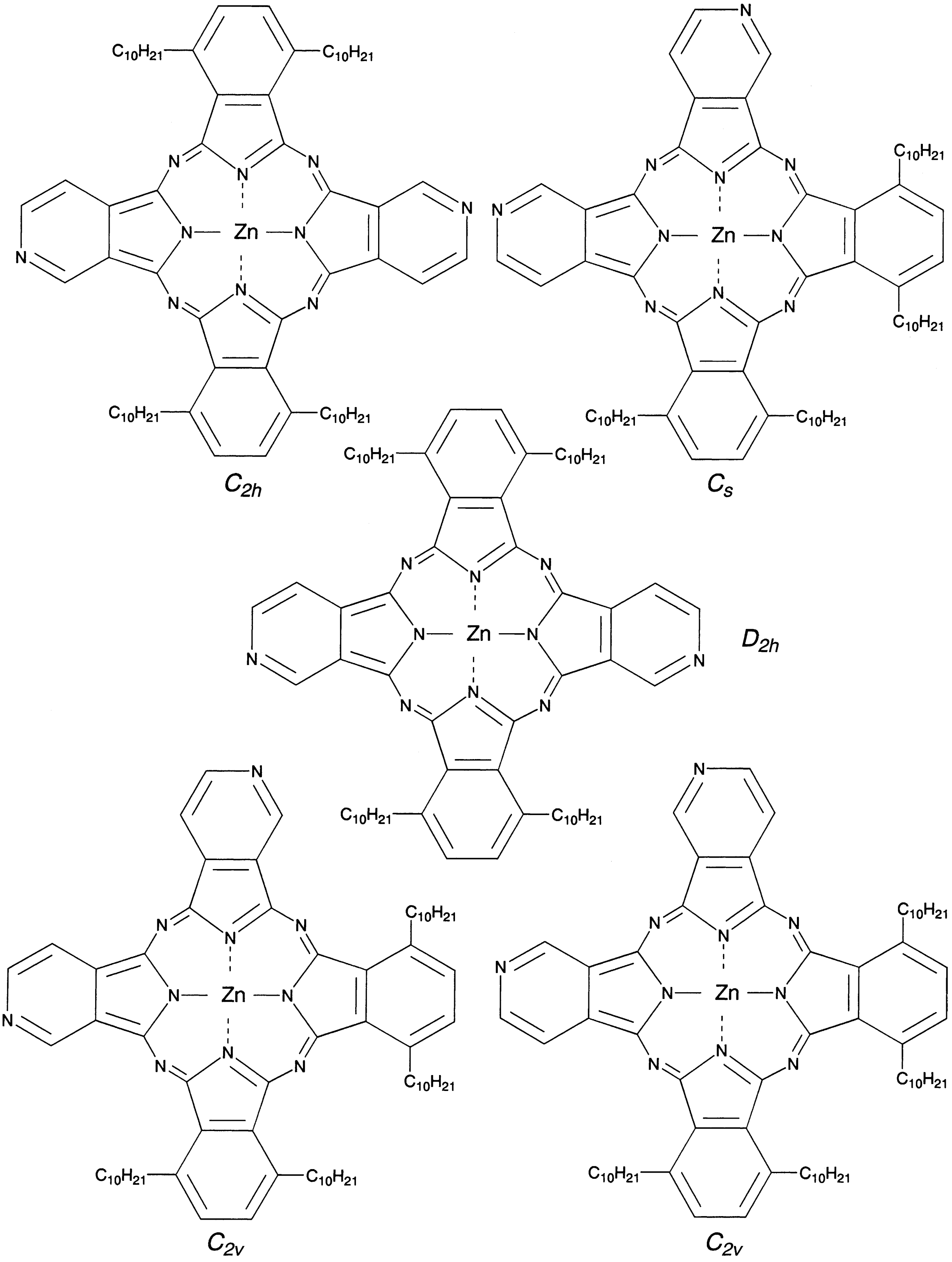
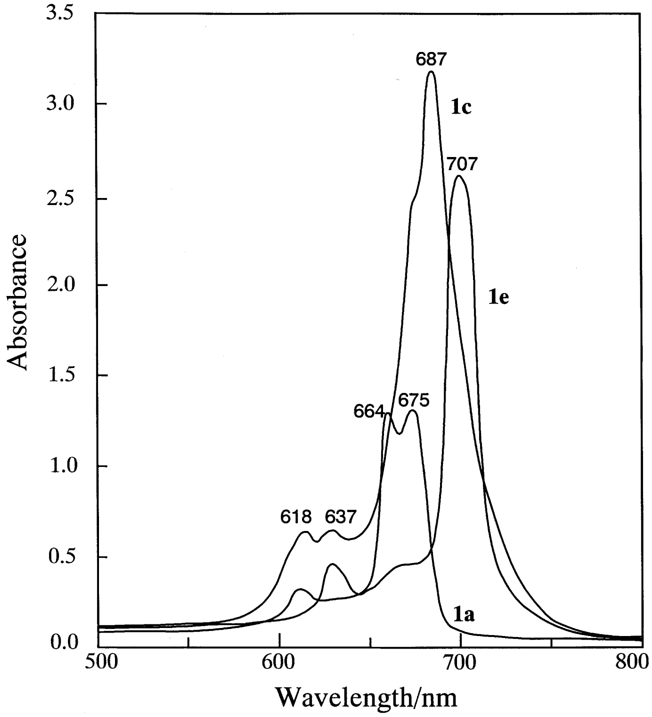


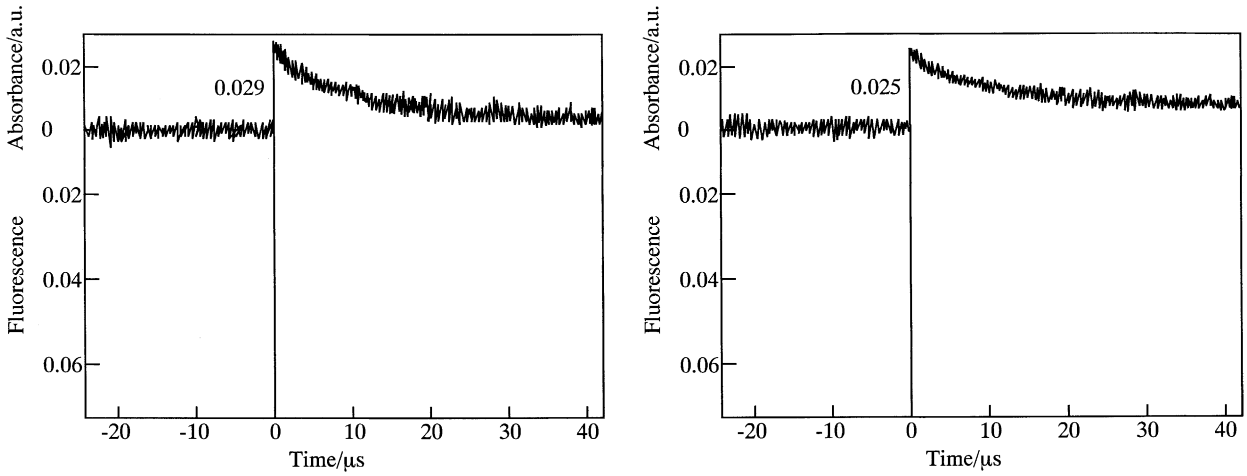
Fig. 2. Molecular structures of position isomers in **1c**.



| Compounds | $\lambda_{max}$ / nm | log $\varepsilon_{max}$ |
|---|---|---|
| 1a* | 675 | 4.243 |
| 1b | 686 | 4.472 |
| 1c | 687 | 4.814 |
| 1d | 686 | 4.661 |
| 1e | 707 | 4.720 |

* Pyridine solution

Fig. 3. UV-Vis spectra of **1a** and **1c** in toluene at $5.0 \times 10^{-5}$ mol dm$^{-3}$, and **1e** in pyridine at $2.6 \times 10^{-5}$ mol dm$^{-3}$.



Non over coat

Covered with polyvinylalchol

Fig. 4. Decay trace of **1c** in PMMA film on 560 nm. Excitation wavelength is 355 nm in the presence and absence of PVA over coatings.

case of being covered with PVA, the photoexited triplet state lifetimes of alkylbenzopyridoporphyrazines, **1b**–**1d** and **1e**, were longer than in the case of non-overcoating with PVA. In the case of non-coated with PVA the shorter decay time was considered due to M-PC quenching by oxygen existing in an air atmosphere. While under the coated state with PVA, they suppressed the oxygen-permeation from the air atmosphere into the photopolymer layer. As a result, grand triplet state dioxigen was not furnished from the surrounding to the system.

Table 1
Triplet lifetime of **1b**–**1e**

| Compound | Q-band in PMMA film (nm) | Lifetime (μs) | |
|---|---|---|---|
| | | Non-over coat | Over coat |
| **1b** | 675.2 | 11.4 | 51.8 |
| **1c** | 717.6 | 10.1 | 46.9 |
| **1d** | 670.0 | 5.7 | 18.2 |
| **1e** | 703.9 | 2.6 | 17.9 |

Alkylbenzopyridoporphyrazines in the case of being covered with PVA behaved as a model for a practical photosensitizer in tumors or cancer cells.

In comparison with **1b** and **1c**, the photoexcited triplet lifetime of **1b** was slightly longer than **1c**, the absorption intensities for **1c** were stronger than **1b**. So that in these aspects, there is little to choose as a sensitizer for PDT between the two. As pyridine rings in the molecule of alkylbenzopyridoporphyrazines increased, the water-solubility is expected to increase. In the case of the $N,N',N'',N''',N''''$-tetramethylated quaternized forms of tetrapyridoporphyrazines, it was reported that the complexes do not form an aggregation in an aqueous solution [13,28,29]. Although the long alkyl-chain substituents in **1b** and **1c** will occur in aggregation, **1b** and **1c** are expected to undergo rapidly photodecomposition after the photooxidation process, similar to alkyl phthalocyanine derivatives [8].

Consequently, since **1b** and **1c** have the most intense absorption and a longer triplet state lifetime, we think **1b** and **1c** will become a useful sensitizer for PDT. The photosensitizer should be made in isomerically pure form [8]. Isomers of **1b** have not been reported yet, but **1c** has been separated and identified [12]. Thereupon, isomers of **1c** were examined by laser-flash photolysis, and **1b** will be reported next time.

### 3.2. *Fractions of* **1c**

The position isomers of the compound, **1c** were separated into four green- to blue-colored fractions by TLC [12]. The four fractions have a different $^1$H-NMR, UV-Vis and fluorescent spectra. The four fractions separated by TLC have been attributed to four of the five possible position isomers of **1c**.

Fig. 5 shows the fluorescence and excitation spectra of **1c**. The excitation spectra of **1c** and its fractions have almost the same profile. No significant change on the fluorescence spectra was observed for **1c** and its fractions.

Table 2 shows the Q-band and fluorescent maximum of fractions of **1c**. The assignment of the Q-band from each fraction was carried out on the theory of the relationship between symmetry and the Q-band [30–33]. The Q-band splits into two peaks of the highest isomer symmetry, the splitting Q-band is decreased with a decreasing symmetry [33]. The symmetry of the position isomer of **1c** was decreased in orders of C$_{2h}$, D$_{2h}$, C$_{2v}$, C$_s$ [10].

Table 2
Absorption and fluorescence maxima for each fraction of **1c** in solution

| Compound | Asorption Q-band (nm) | Fluorescence (nm) | Symmetry |
|---|---|---|---|
| Fraction 1 | 627, 690[a], 705[b] | 704 | D$_{2h}$ |
| Fraction 2 | 609, 673[b], 708[a] | 706 | C$_{2h}$ |
| Fraction 3 | 619, 689[b] | 695 | C$_s$ |
| Fraction 4 | 610, 638, 671[b], 688[a] | 701 | C$_{2v}$ |

[a] Next intense peak.
[b] Most intense peak.

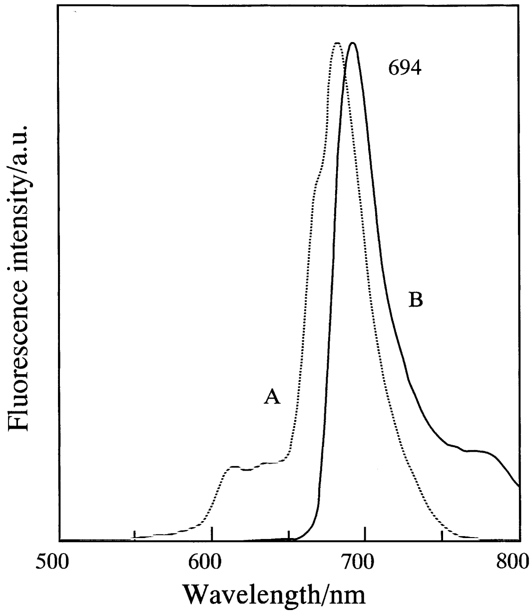


Fig. 5. Fluorescence and excitation spectra of **1c** in DMF. A: Excitation spectrum; B: fluorescence spectrum.

The position isomers of **1c** were the symmetry of molecular structures as D$_{2h}$, C$_{2h}$, C$_s$ and C$_{2v}$ for fractions 1, 2, 3 and 4, respectively [12]. Two types of C$_{2v}$ isomers were not able to be isolated [12].

Table 3 shows the photoexcited triplet lifetime of fractions separated from **1c**. In spite of the presence or absence of PVA coatings, the triplet lifetime was increased with a decreasing symmetry of position isomers, which were ordered as C$_{2h}$, D$_{2h}$, C$_{2v}$ and C$_s$ for fractions 2, 1, 4 and 3, respectively. The photoexcited triplet state lifetimes of fraction 3 in PMMA absence and presence of a PVA coating were estimated to be 14.29 and 25.97 $\mu$s, respectively. Of each fraction except for fraction 3, the length of the lifetime was shorter than **1c**, and the sensitivities of triplet–triplet (T–T) absorptions were observed as very low.

Although the length of the triplet lifetime of **1c** was observed by approximately four times that of the absence of a PVA over coating, the fractions of **1c** were only about 1.5 times as long as triplet lifetimes in comparison with the absence and presence of PVA coatings.

Unfortunately, a precise solution to the cause cannot be obtained. However, it seems to be the followings. Phthalo-

Table 3
Triplet lifetime of each fraction of **1c**

| Compound | Q-band in PMMA film (nm) | Lifetime ($\mu$s) | |
|---|---|---|---|
| | | Non-over coat | Over coat |
| Fraction 1 | 728.2, 681.6, 653.5 | 7.0 | 11.3 |
| Fraction 2 | 670.0 | 0.9 | 1.6 |
| Fraction 3 | 696.4 | 14.29 | 25.97 |
| Fraction 4 | 665.5 | 6.4 | 9.2 |

Table 4
Triplet lifetime of each fraction of **1c** using Micher's keton as a quencher

| Compound | Lifetime (μs) | |
|---|---|---|
| | Non-over coat | Over coat |
| Fraction 1 | – | – |
| Fraction 2 | – | – |
| Fraction 3 | 21.19 | 72.72 |
| Fraction 4 | 14.03 | 47.32 |

cyanine derivatives were well known to aggregate in water and non-coordinating solvents. Zinc non-peripheral phthalocyanine derivatives having long side chains formed an aggregation at least $10^{-5}$ mol dm$^{-3}$ in cyclohexane [8,34]. It is enough thought that the samples in this study for laser-flash photolysis were formed in aggregation in the experimental condition. The aggregation degree for **1c** and its isomers is different from each other. And then, the ability of aggregation for **1c** and each of its isomers is a difference and complication. Since compounds **1b** and **1c** were consisted mixtures of their isomers, the aggregation and relationships of the energy levels between samples and the triplet state of dioxygen became a complication. For this reason, compounds **1b** and **1c** could measure relatively long lifetimes. The molecular structure of fraction 3 is suitable to occur in the T–T absorption in the system.

In order to estimate the photoexcitation mechanism, the triplet lifetime of each fraction was measured, containing *N*,*N*′-tetramethyl-4,4′-diaminobenzophenon (Micher's keton) as an additional quencher. As using Micher's keton, the lifetimes without PVA coatings were estimated as 21.19 and 14.03 μs for fractions 3 and 4, respectively (Table 4). These values of lifetime were longer than in the absence of Micher's keton. In the case of fractions 1 and 2, no T–T absorption occurred. The results were thought to be that each fraction has different energy levels of grand and excited states. The T–T absorption took place via the interactions between the energy levels of grand or excited states of fractions and the triplet of dioxygen or Micher's keton.

## 4. Conclusion

The triplet state of zinc non-peripheral substituted alkylbenzopyridoporphyrazines was measured using laser-flash photolysis in PMMA film.

The triplet lifetimes of alkylbenzopyridoporphyrazines increased with an increasing pyridine number in the molecule. One of the zinc non-peripheral substituted alkylbenzopyridoporphyrazines, zinc dibenzo-di(3,4-pyrido)porphyrazine, **1c** in the PMMA layer showed the most intense absorption and a longer triplet state lifetime. The photoexcited triplet state lifetimes of **1b** and **1c** in PMMA without a PVA coating were estimated to be 11.4 and 10.1 μs, respectively. While covered with a PVA coating, the photoexcited triplet state lifetimes of **1b** and **1c** were estimated as 51.8 and 46.9 μs, respectively. The compound **1c** was suitable for use of the sensitizer for PDT, since **1c** has the most intense absorption and a longer triplet state lifetime.

The triplet lifetime for position isomers in **1c** was increased with the decreasing symmetry of position isomers, which were ordered as $C_{2h}$, $D_{2h}$, $C_{2v}$ and $C_s$ for fractions 2, 1, 4 and 3, respectively. The photoexcited triplet state lifetime of fraction 3 in PMMA in the absence and presence of PVA coatings were estimated to be 14.29 and 25.97 μs, respectively.

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